

Instrumental considerations for reliable fieldable VOC analyses

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Abstract

The major justification for field analysis is the production of data and information that allows decisions to be made in a timely fashion for effective mitigation and/or efficient remediation of environmental contamination. Secondary benefits include lower cost per sample, more samples analyzed per work shift, and improved monitoring for worker safety. However, all of these applications require production of field analytical data of high quality and documented consistency and integrity. These data quality requirements place special constraints on the analytical instruments that are used for field analysis. The application and analytical capabilities of a dual silicon micro fabricated gas chromatographic instrument, with dedicated microprocessor control of all analytical functions, are discussed in relation to fieldable analytical chemistry. This small, rugged and very fast instrument provides for redundancy in analytical results, or, alternatively, the use of different modes of separation to achieve a wide variety of analytical capabilities within a portable instrument configuration.

Keywords: Field analysis; Instrumentation; On-site

1. Introduction

Traditional environmental assessments and clean-up strategies for responding to chemical spills and/or uncontrolled releases from hazardous waste sites include using various survey and sampling technique, laboratory chemical analysis, and access to information in toxicological and environmental databases. Assessment information is used to develop a remedial plan which can be implemented with appropriate response and/or engineering technologies (absorption, solidification, incineration, bioremediation, land farming, etc.). Following remedial clean-up, the site can be declared safe ("closed") after data from appropriate laboratory chemical analyses are examined and

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used to confirm that the chemical hazards have been removed, destroyed and otherwise reduced.

This traditional approach, relying on fixed laboratory chemical analytical support, is very costly, time consuming, and may not allow for effective and timely removal or reduction of the toxic chemical problems at these sites [1]. Relatively new techniques, collectively known as fieldable analytical chemistry, can be useful in helping to optimize the investigative, assessment, and remedial activities associated with responding to uncontrolled and/or unanticipated releases of hazardous chemicals [2]. Effective chemical hazard assessments and the development and implementation of mitigative actions require timely access to information on the identities and quantities of hazardous chemicals. Acute hazards most often result from volatile airborne contaminants that can either explode, burn, or cause exposure through inhalation pathways. Without the ability to provide rapid, on-site analytical support, effective chemical hazard assessments are either overstated (resulting in excessive response measures) or speculative (resulting in inappropriate response measures). Further, fieldable analytical chemistry can be used in the remedial portion of site clean-up activities to provide near real-time analytical support for both monitoring on-site hazards and directing various operational aspects of the remedial technology. Portions of the Superfund Amendments and Reauthorization Act of 1986 (SARA) and the new Clean Air Act also require fieldable (on-site) analytical instrumentation for monitoring of specific volatile organic compounds (VOC's) in heavily industrialized and urbanized areas.

On-site analysis, in its broadest sense, can be performed using conventional instruments in mobile laboratories or with portable and/or transportable instruments [3]. The primary focus of this discussion will be on the analytical characteristics of portable battery powered fieldable instruments for analysis of organic environmental contaminants. Also, since portable instruments, by their very nature, need to conserve power, not all analytical zones that come in contact with the sample can be heated. The practical implication of not heating all sample zones is that the battery powered instruments are limited to analyzing organic compounds that have ambient temperature vapor pressures of 1 mm of Hg or greater. This vapor pressure limit corresponds to compounds with Kovats retention indices of 1000 or less [4]. Consequently, this discussion will be focused on fieldable analysis of volatile organic compounds (VOC) with portable analytical instruments.

The aims of fieldable VOC analytical chemistry are to help solve important environmental problems with: (a) fieldable analytical instruments; (b) fieldable analytical methods and procedures together with appropriate QA/QC guidelines; and (c) techniques to enhance the information content and analytical results of sampling procedures. The primary objective of fieldable analytical chemistry is to use high quality analyses, outside of standard laboratory settings, for quantification of target compounds in environmental samples. The analytical information produced from these target compound analyses can be used in near real time to facilitate effective chemical hazard assessments and mitigative actions during: (a) emergency responses to chemical spills; (b) remedial investigations and feasibility studies of hazardous waste sites; (c) removal operations at hazardous waste sites; (d) special investigative

operations such as drum and tank head-space analysis; (e) soil gas analysis and fence line monitoring; (f) point source emission monitoring; and (g) fugitive emission monitoring.

2. Discussion

Clearly, effective fieldable VOC analytical chemistry is a process that includes the generation of high quality analytical data, conversion of data into chemical information, and the use of the information to assess hazards and/or develop and implement mitigative strategies to solve environmental problems. This implies that fieldable instruments, procedures, and sampling methods should have the analytical, operational and value-added characteristic as outlined in Table 1. It is important to point out that these general characteristics are greatly influenced by application specific requirements. However, all of these features are desirable, to some extent, in fieldable VOC instrumentation. For example, some applications will require low detection limits of a relatively few analytes while other applications will need higher resolution to distinguish elevated levels of complex mixtures. The ideal fieldable instrument will have the analytical flexibility to be useful in these diverse applications.

Table 1
Important characteristics for fieldable VOC analytical instruments

Analytical capability
(1) Selectivity
(2) Resolution
(3) Peak capacity
(4) Analyte range
(5) Sensitivity and detection limits
(6) Precision and accuracy
Operational parameters
(1) Speed
(2) Size/transportability
(3) Power and utilities consumption
(4) Ease of use
(5) Level of operator skill required for effective use
(6) Reliability/ruggedness
(7) Cost
Value added features
(1) Ability to produce chemical information
(2) Use of peer accepted and QA/QC procedures
(3) Reliability of manufacturer
(4) Accessibility (lots of devices in use)
(5) Wide range of applications (2 or 3 possible applications per device)
(6) Access to service, availability and quality of manual
(7) Adaptability to other applications
(8) Use of state-of-the-art technology
(9) Access to and quality of technical support

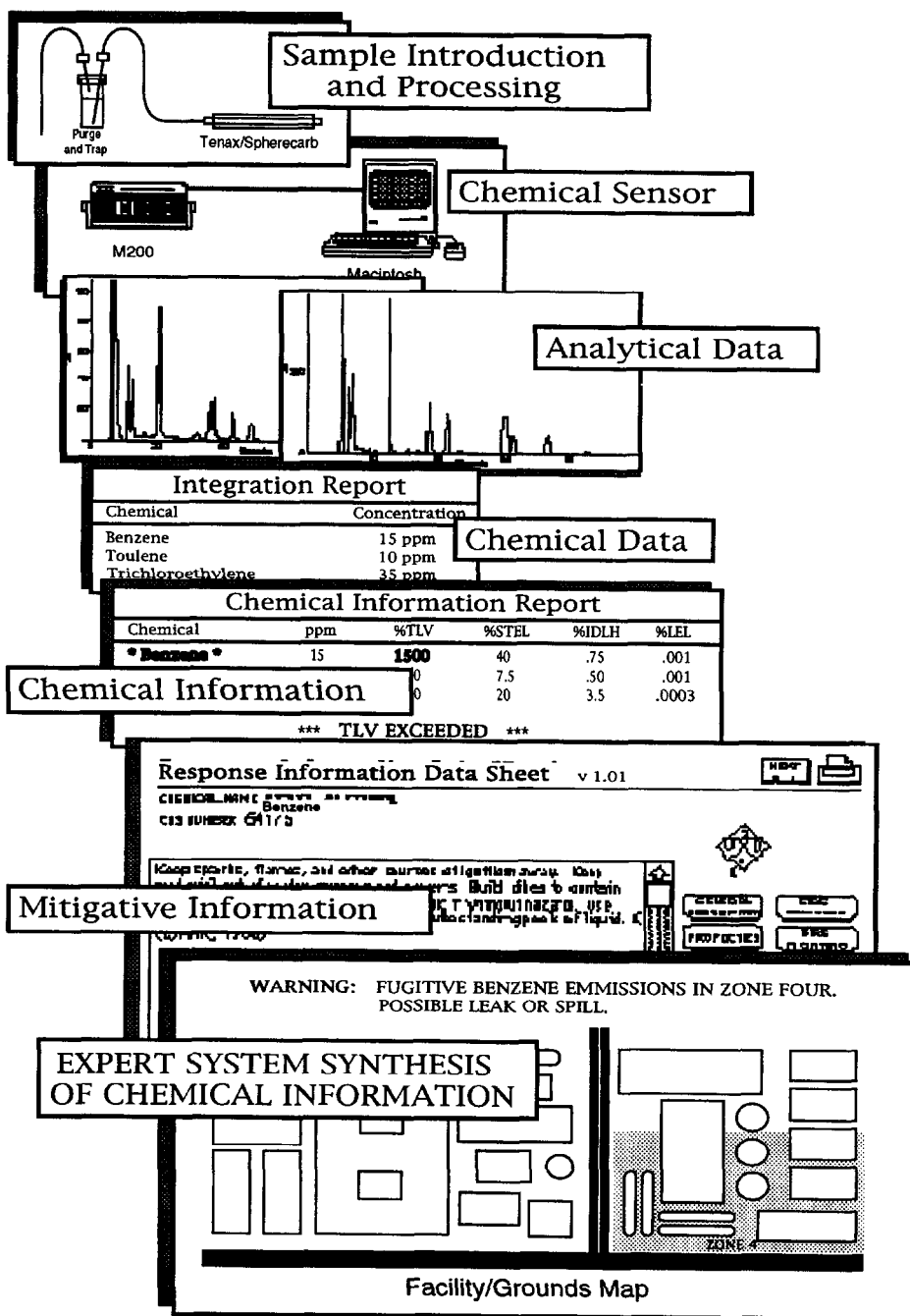


Fig. 1. Problem solving analytical instrument. Diagram of the steps involved in effectively using fieldable analytical chemistry to solve environmental problems including analysis of the sample, production of analytical and chemical data, conversion of this data into chemical or mitigative information or other formats that are useful in the decision making process.

Fieldable VOC analyses are used to produce analytical information appropriate for management decisions. There are several essential steps, outlined in Fig. 1, that are needed for production of analytical information useful for the development of mitigative strategies or risk assessments from fieldable VOC analytical chemistry. Basically, they include operation of a fieldable analytical instrument (a chemical sensor) to produce *analytical data* (i.e., gas chromatograms or mass spectra). The analytical data must be converted to *chemical data* (identities and concentrations of specific compounds) using appropriate data systems and software, use of reference standards, and/or intuition of the operator. These steps must include the use of appropriate quality assurance and control procedures. Chemical data must then be synthesized into *chemical information* and/or *mitigative actions*, a process known as chemical hazard assessment, by integration of the chemical data with information in chemical and toxicological databases. This latter process is currently carried out by appropriately trained response personnel and is the basis upon which management decisions are made.

With access to powerful and compact portable computers, the process of integration of chemical data with database information will become automatic. In the near future, fieldable analytical devices will yield chemical information and/or mitigative actions in much the same fashion as current analytical systems produce chemical data. This automation in the production of chemical information and mitigative actions will place special and important constraints on the quality of fieldable chemical instruments and procedures as well as the data acquisition and treatment software (i.e., the analytical data producers). These constraints are needed to ensure that the chemical identities and quantitations reflect the compositions of the samples. It is important to note here that relatively small errors in identification or quantitation (e.g., inability to distinguish between benzene, chloroform, and carbon tetrachloride based on their nearly identical retention times or small differences in the mass spectra of similar compounds) will be automatically propagated and embellished by computer conversion of faulty analytical data into faulty chemical information and/or mitigative actions. Consequently, fieldable analytical instruments that automatically produce risk assessment information from analytical data must have a high degree of capability and inherent integrity designed into their analytical functioning.

The introduction of micromachined gas chromatographic instrumentation in the late eighties provided an analytical device with many of the characteristics of an idealized fieldable analytical instrument. Key components of this type of analytical device were fabricated by micromachining on a silicon wafer valves, tubing, flow restrictions, connection points, and a very small internal volume thermal conductivity detector. The analytical columns are external to the wafer and the valves are operated by pneumatic pressure actuated from an external manifold. Both analog and digital electronics are on conventional PC boards. A key design of the microchip gas chromatograph is that a dedicated microcontroller operates all timing sequences, temperature controls and valve operations as well as digitization of data for processing by an external microcomputer [5].

Fig. 2 outlines the functional components of microchip GC instruments. When the sample microvalve opens, a gaseous sample is pumped through the 11 μl sample loop.

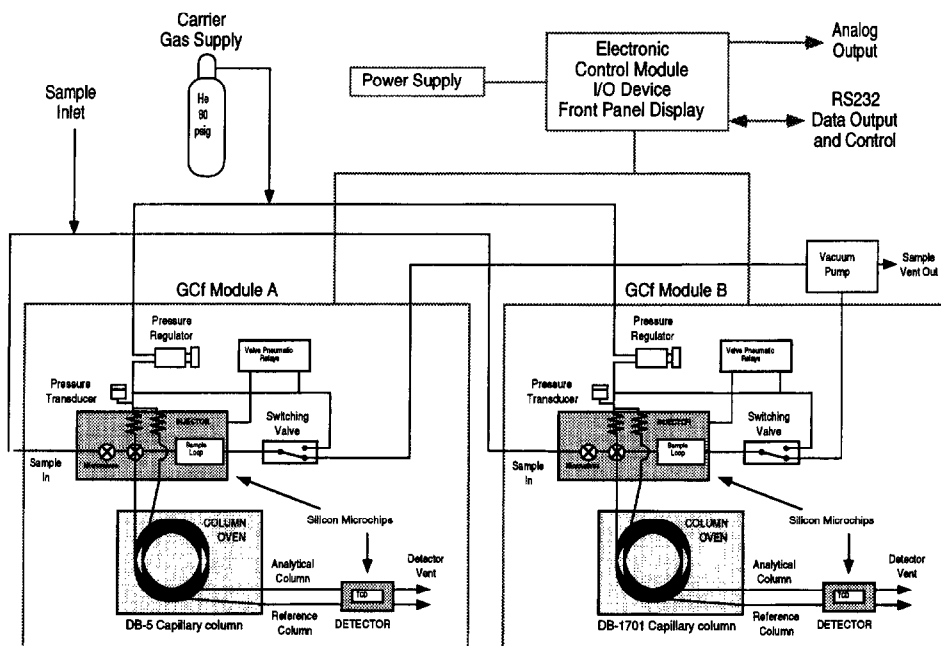


Fig. 2. Functional diagram of Michromonitor 200 Dual Microchip GC. Functional diagram of a microfabricated gas chromatograph instrument containing two independently operated high resolution GC modules. The injectors and detectors were micromachined on silicon wafers while the columns, pneumatic solenoids and electronic circuits are external to the wafers.

After sample introduction into the sample loop, the sample valve closes and the sample loop is pressured with carrier gas thus compressing the sample into the front portion of the sample loop. The injection valve is then opened for, typically, 250 ms injecting the compressed sample onto the analytical column. The columns can be either open tubular or micropacked with the latter used for analyses of the permanent gases and the former used for VOC applications. The columns are isothermally controlled at temperatures between ambient and 180 °C every 200 ms to a precision of a tenth of a °C. Eluting compounds are detected in a very small internal volume thermal conductivity detector. Data are digitized at 100 Hz and processed by an external data system. The instruments are completely under the control of an imbedded microcontroller allowing unprecedented precision in the timing of analytical sequences, valve operations, and in temperature control during analyses. Two nearly identical instruments are commercially available from MTI Analytical Instruments, Fremont CA and Chrompack International, Raitan NJ.

The microchip gas chromatograph is an instrument that has virtually all of the desired characteristics listed in Table 1 for state-of-the-art fieldable analytical instruments. Each instrument contains two separate gas chromatographic modules making the instrument, in essence, a dual microchip high resolution gas chromatographic

analyzer. The use of two separate chromatographic modules in one instrument has several distinct advantages when compared to conventional fieldable gas chromatographic analyzers. Two very high resolution narrow bore capillary columns allows identifications to be based on retention behavior of separated peaks on two columns of similar length and bore but with different liquid phases. Table 2 provides retention indices, based on the normal hydrocarbon index scale, for compounds of environmental interest analyzed with microchip GC modules containing 4 m, 100 μm OV 73

Table 2
Retention indices on microchip GC modules with OV-73 and OV-1701 liquid phases

Name	RIA	RIB
1,1,1,2-tetrachloroethane	852.9	922.9
1,1,1-trichloroethane	652.8	694.3
1,1,2,2-tetrachloroethane	914.7	1035.2
1,1,2-trichloroethane	775.6	869.9
1,1,2-trichlorotrifluoroethane	529.8	539.9
1,1-dichloroethane	583.5	646.9
1,1-dichloropropene	662.5	701.1
1,2,3-trichloropropane	921.5	1029.5
1,2-dichloroethane	655.5	736.3
1,2-dichloropropane	704.5	775.0
1,3,5-trimethylbenzene	968.1	1016.9
1,3-dichloropropane	788.9	876.6
1,4-dioxane	718.2	789.9
1-nitropropane	745.2	874.8
2,2,4-trimethylpentane	689.8	689.5
2,2-dichloropropane	620.6	671.1
2-chloroethyl vinyl ether	733.8	812.4
2-methoxyethanol	649.3	752.9
2-nitropropane	705.0	826.1
2-pentanone	694.1	781.1
2-picoline	849.1	917.2
acetic acid	618.7	789.5
acetone	500.1	594.1
acetonitrile	496.4	630.5
acrolein	491.3	578.6
acrylonitrile	530.6	647.4
air	145.2	286.6
benzene	669.4	719.0
bromobenzene	930.8	999.0
bromochloromethane	624.2	699.0
bromodichloromethane	712.4	794.5
bromoform	887.8	984.3
butane	400.0	400.0
carbon disulfide	552.0	578.2
carbon tetrachloride	669.9	695.9
chlorobenzene	850.2	912.2

(continued on next page)

Table 2 (Continued)

Name	RIA	RIB
chlorodibromomethane	800.4	890.4
chloroethane	451.2	496.7
chloroform	623.7	698.9
cis-1,2-dichloroethylene	613.6	680.4
cis-1,3-dichloropropene	744.4	816.4
cumene	925.5	972.8
cyclohexane	669.5	680.2
cyclohexanone	903.0	1011.8
cyclohexylamine	669.3	679.9
cyclopentane	572.7	583.0
dibromomethane	708.1	787.9
dichloromethane	539.2	610.8
dimethylamine	541.7	578.1
epichlorohydrin	725.9	829.9
ethyl acetate	619.5	681.4
ethyl alcohol	459.6	561.5
ethyl benzene	864.9	914.2
ethyl bromide	530.8	583.8
ethyl ether	509.0	533.4
ethyl formate	521.3	586.9
ethylene dibromide	811.2	893.4
formaldehyde	525.2	568.4
furan	503.8	550.5
heptane	700.0	700.0
hexane	600.0	600.0
iso-amyl acetate	882.8	944.4
iso-amyl alcohol	743.0	849.2
iso-butyl acetate	779.6	840.6
isobutyl alcohol	634.3	737.3
isoprene	511.6	534.2
isopropanol	503.1	600.1
<i>m</i> -xylene	872.1	921.6
methanol	388.7	493.5
methyl ethyl ketone	604.0	692.6
methyl isobutyl ketone	747.6	830.3
methyl <i>t</i> -butyl ether	576.2	603.2
<i>n</i> -amyl acetate	920.5	983.6
<i>n</i> -butanol	672.9	777.0
<i>n</i> -butyl acetate	820.3	883.0
<i>n</i> -propyl benzene	953.5	1002.4
nonane	900.0	900.0
<i>o</i> -chlorotoluene	950.8	1009.3
<i>o</i> -xylene	895.2	949.6
octane	800.0	800.0
<i>p</i> -chlorotoluene	956.4	1020.2
<i>p</i> -xylene	872.7	921.6
pentane	500.0	500.0
propyl alcohol	566.0	669.5
pyridine	776.6	856.5

Table 2 (Continued)

Name	RIA	RIB
sec-butyl acetate	765.2	822.7
styrene	893.2	957.7
tert-butyl acetate	708.3	757.0
tetrachloroethylene	814.0	843.0
tetrahydrofuran	641.7	695.6
toluene	772.3	822.3
trans-1,2-dichloroethylene	569.5	614.2
trans-1,3-dichloropropene	769.1	856.0
trichloroethylene	704.9	749.1
trichlorofluoromethane	490.1	508.7
vinyl acetate	585.1	648.3
vinyl chloride	392.4	426.8
vinylidene chloride	525.6	558.2
water	339.9	449.7

and OV1701 analytical columns at 60 °C. Typical analysis times are under 2 min with isothermal peak widths for the early eluters of several hundred milliseconds and a second or two for late eluting compounds. Therefore, with the use of two microchip chromatographs simultaneously analyzing the same sample, the compound identification function, in essence, has both resolution and selectivity (from redundant analyses) as well as speed. All other fieldable VOC analytical devices rely on compound identifiers using either a single rather low resolution column, or a single beam or single wavelength IR spectrometer subjected to interferences, or a very expensive, complex and power hungry mass spectral detector. It is important to emphasize here that accurate quantitative analyses of target analytes must be preceded by instrumental selectivity that produces reliable qualitative determinations. Therefore, use of the microchip GC's selectivity and resolution are important characteristics for a field deployable analytical device.

With microchip GC instruments, selectivity and speed advantages come at the cost of elevated detection limits. Since only a microliter or less of the sample is injected onto the analytical column, detection limits of the microchip GC modules are around 1 ppmv. This corresponds to detection of 40 femtomoles or low picogram quantities of analytes (4 pg of compounds with a molecular weight of 100) by the micro thermal conductivity detector. However, since only a microliter was injected, instrumental detection limits are in the low ppmv range. Method detection limits can be considerably lowered by concentrating analytes on solid sorbent traps prior to desorption and analysis with the microchip GC instrument [6]. Fig. 3 shows analysis of a 10 ppbv air sample containing benzene, toluene, ethylbenzene and *m*-xylene. Clearly, when used with appropriate sample concentrating devices, the fieldable microchip GC can have method detection limits near 1 ppbv while providing both enhanced speed and selectivity characteristics to the analytical process [7, 8]. Other approaches, using either a sensitive but low resolution identifier such as a photo ionization detector, or

Three Consecutive 10ppbv BTEX runs- 1 liter sample volumes

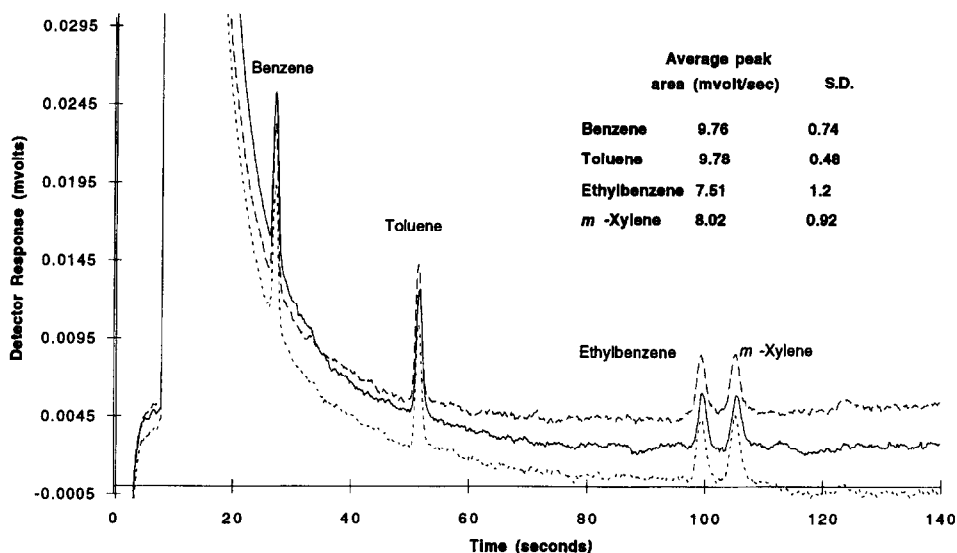


Fig. 3. Three consecutive 10 ppbv BTEX runs – 1 l sample volumes. Triplicate microchip gas chromatograms from analysis of a 10 ppbv air sample containing benzene, toluene, ethylbenzene and *m*-xylene on a 4 m, 0.1 mm OV-73 column with a micro thermal conductivity detector. 1 l of the sample was adsorbed onto a tenax-spherocarb trap prior to being thermally desorbed into the microfabricated sample loop of the microchip GC module.

a very complex and technically sophisticated identifier, such as a mass spectrometer, seems to be using technologies that are not optimally compatible with the desirable characteristics of the idealized field deployable analytical device as identified in Table 1.

Having two separate microchip gas chromatographic modules has other advantages in addition to selectivity and speed. Each module can be operated with appropriate liquid phases, lengths, flow rates and temperatures to allow analysis of a variety of analytes with widely different volatilities. Alternately, using different temperatures with each module can significantly reduce analysis time. Also, a combination of micropacked and open tubular columns can allow analysis of permanent gases simultaneously with VOCs. Having two separately operated gas chromatographs within a single instrument provides flexibility unparalleled in conventional fieldable instruments. Fig. 4 shows data from microchip GC analysis of a contaminated industrial soil sample containing vinyl chloride (VC) and ethylene dichloride (EDC). By operating one module at elevated temperatures (80 °C) and the other at 40 °C, both vinyl chloride and EDC were unequivocally and selectively quantitated with total run times of around 50 s. Rapid run times translate directly into either lower cost per sample or more samples analyzed during a given work day.

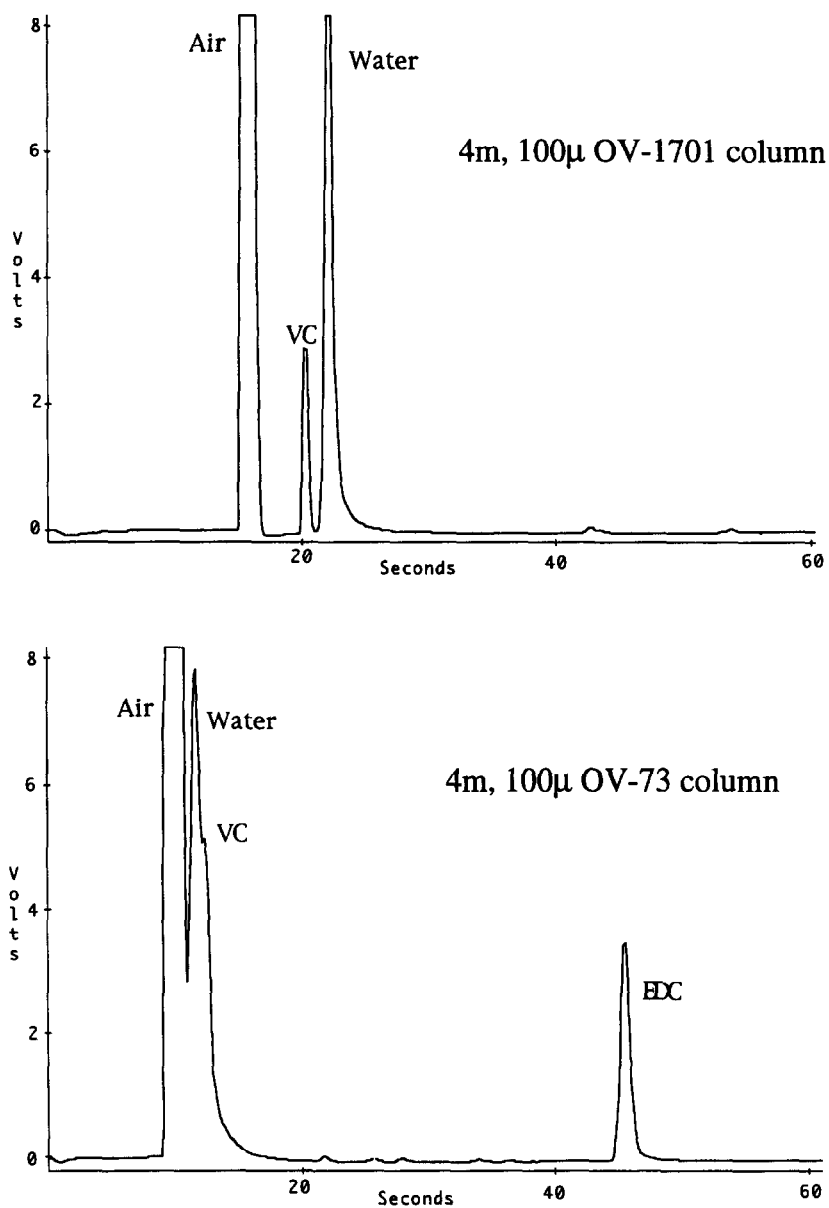


Fig. 4. Microchip GC analysis of the head space of a contaminated soil from an industrial location. The top chromatogram was run on a module containing a 4 m, 0.1 mm OV-1701 column operated at 40 °C isothermal while the bottom chromatogram was run simultaneously on a module containing a 4 m, 0.1 mm OV-73 column operated at 80 °C. The nonpolar OV-73 column does not have sufficient polarity to separate the air and water peaks allowing detection of vinyl chloride while the OV-1701 column provides baseline separation between vinyl chloride and water. Analysis of both vinyl chloride and ethylene dichloride were thus achieved in less than 1 min run time.

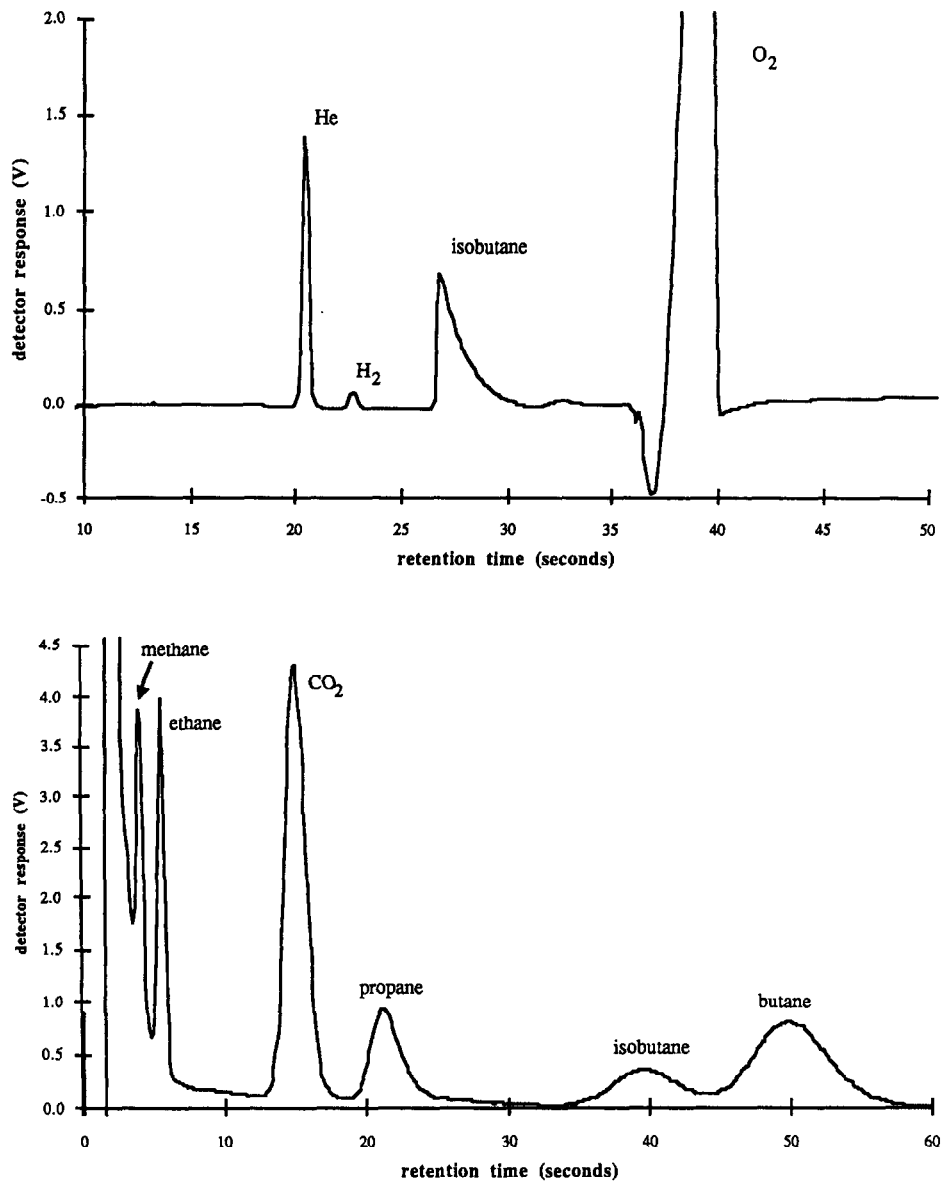


Fig. 5. Microchip GC analysis of the head space of a crude oil sample taken from a salt dome oil storage cavern showing analysis using both gas-solid chromatographic separation mechanisms with PLOT and micropacked columns. The top chromatogram was obtained using a microchip GC module with a 10 m, 0.32 mm Molecular Sieve 5A PLOT column while the bottom chromatogram was run on a module containing a 25 cm Haye Sep A micropacked column.

Alternately, the microchip GCs may be configured with one module using a micro-packed column, such as with a 5 A Molecular Sieve material using nitrogen as a carrier, while the other module contains a open tubular column coated with a nonpolar liquid phase (OV-1) using helium as the carrier gas to enhance the sensitivity towards hydrocarbon vapors with the thermal conductivity detector. Fig. 5 shows data from microchip GC analysis of the head space from crude oil taken from an underground salt dome oil storage cavern. The entire analytical sequence takes less than a minute and provides data on the very light hydrocarbon gases as well as the noble gases, hydrogen, and carbon dioxide. There are many other applications, including in situ bioremediation and bioventing, which need analytical responses over a similar wide range of analyte volatilities. The dual microchip GC instrumentation is ideally suited for these diverse types of applications which would otherwise require two or more analytical devices to achieve the same results.

3. Conclusions

In summary, microfabricated analytical instrumentation relies on dedicated micro-processor real time control of all timing and temperature control functions. This results in small, rugged analytical devices that exhibit incredible precision in their analytical functioning. The small size has the added advantage that two or more separate gas chromatographic modules can be combined into a single analytical instrument. Dual analytical capability provides built-in redundancy, a choice in separation modes and columns, and a wide dynamic range for analyte with vastly differing volatilities. All of these characteristics are desirable for fieldable analytical instrumentation to ensure data quality.

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